

**Measurements of the Thermal Conductivity of R134a in the
Temperature Range from 300 to 460 K and at Pressures up to 45 MPa¹**

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¹ Paper presented at the Thirteenth Symposium on Thermophysical Properties,
June 22-27, 1997, Boulder, Colorado, U.S.A.

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ABSTRACT

We report the measurements of the thermal conductivity of R134a with a coaxial cylinder cell operating in the steady states. The measurements of the thermal conductivity of R134a were performed along several quasi-isotherms between 300 and 460 K, in the gas phase, the liquid phase and the critical region. The pressure range covered varies from 0.1 to 45 MPa. A careful analysis of the various sources of errors leads to an estimated uncertainty of the measurements ranging from 1 and 2 %.

KEY WORDS: thermal conductivity, critical region, R134a

1. INTRODUCTION

Recently they have been a great interest in the determination of the thermophysical properties of R134a (1,1,1,2-tetrafluoroethane), an environmentally acceptable alternative refrigerant to R12 (dichlorodifluoromethane). The previous measurements of the thermal conductivity of R134a revealed significant discrepancies from each other. These discrepancies are much larger than the respective accuracy claimed by the various authors. The thermal conductivity of R134a was measured in vertical coaxial cylinders, operating in the steady-state mode. The same apparatus was already used in the measurement of the thermal conductivity of 1-chloro-1,1-difluoroethane (H C F C - 142b) [1]. The purity of the sample is 99.9%. The measurements were performed in order to make an analysis of the data based on the residual concept. The transport property surface is separated into three different regions, the gaseous state (at $P = 1$ atm.), the dense state and the supercritical region ($T > T_c$).

2. DILUTE-GAS THERMAL CONDUCTIVITY

The results of the measurement of the thermal conductivity at atmospheric pressure. are presented in table I. The experimental data were fitted to a linear equation

$$\lambda_o = -14.1875 + 0.0905 T \quad (1)$$

The temperature dependence of the thermal conductivity of the dilute gas can be represented by an expression derived from the kinetic theory of gases. The thermal conductivity is related to the reduced effective collision cross sections Ω_λ^* which contains all the contributions from translational, rotational, vibrational and electronic degrees of freedom. As there is a lack of reliable experimental data on vibrational collision number

we used for the calculation of the thermal conductivity in the zero density the practical engineering form

$$\lambda_o(T) = \frac{0.177568(T/M)^{0.5} C_p^o / R}{\sigma^2 \Omega_\lambda^*} \quad (2)$$

where $T^* = kT/\varepsilon$, Ω_λ^* is the reduced effective collision cross-section for thermal conductivity and C_p^o , is the ideal isobaric heat capacity. The scaling factors σ and ε/k which correspond to the Lennard-Jones 12-6 potential parameters were determined by Wilhelm and Vogel [2] from a fitting of their viscosity data of R134a ($\varepsilon/k = 288.82$ K and $\sigma = 0.50647$ nm). The ideal specific heat at constant pressure was calculated by

$$C_p^o = \sum_{i=0}^6 c_i T^{i-1} \quad (3)$$

where

$$c_0 = 29.897917, \quad c_1 = 0.1258739, \quad c_2 = 5.0253157 \times 10^{-4}$$

$$c_3 = -1.2811 \times 10^{-6}, \quad c_4 = 1.144944 \times 10^{-9}, \quad c_5 = -3.847382 \times 10^{-13}$$

$$c_6 = 1.1471368 \times 10^{-17}$$

The maximum deviation between Eq. (1) and the theoretical values calculated by Eq. (2) was found to be less than 0.5% from 317 K to 490 K. The agreement which is good up to 700 K, shows that Eq. (1) can be extrapolated up to this temperature

2. DENSE FLUID THERMAL CONDUCTIVITY

In order to determine the excess function or the residual term of the thermal conductivity $\Delta_R \lambda(\rho, T)$, we have performed measurements in the liquid phase and in the gas phase far away from the critical region along six quasi isotherms at 302 K, 321 K, 331

K, 349 K, 443 K and 463 K. Experimental results are reported in tables II - VII.. The deviation is always less than the experimental uncertainty. The excess function of the thermal is represented by a six-order polynomial of the form

$$\frac{\Delta_r \lambda}{\Lambda_c} = \sum_{i=1}^6 b_i \left(\frac{\rho}{\rho_c} \right)^i \quad (4)$$

where $\rho_c = 508 \text{ kg m}^{-3}$, is the critical density and

$$\Lambda_c = \frac{R^{5/6} P_c^{2/3}}{T_c^{1/6} M^{1/2} N_A^{1/3}} = 2.055 \text{ mW m}^{-1}\text{K}^{-1} \quad (5)$$

The coefficients b_i in Eq.(4) are

$$b_1 = 4.483744 \quad b_2 = 3.514431 \quad b_3 = 5.845843$$

$$b_4 = -8.455823 \quad b_5 = 3.835369 \quad b_6 = -0.5335625$$

In the last column of the tables the deviations between experimental and calculated values using the background equations of the thermal conductivity of R134a are reported. The deviation is always less than the experimental uncertainty.

3. THERMAL CONDUCTIVITY IN THE CRITICAL REGION

Around the critical density the well-known enhancement of the thermal conductivity was observed. This critical enhancement of the thermal conductivity $\Delta_c \lambda(\rho, T)$ was carefully measured, a comparison is given in Table VIII at the critical density with the values calculated by Krauss et al. from thermal diffusivity data[3].

ACKNOWLEDGMENTS

We are indebted to R. Krauss for providing us with his computer program of transport properties of R134a.

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Table I. The thermal conductivity of R134a at atmospheric pressure

T (K)	299.18	301.71	316.53	330.19	337.55	345.03	348.56
λ (mW.m ⁻¹ .K ⁻¹)	12.76	13.12	14.46	15.63	16.28	17.06	17.43

T (K)	351.24	357.95	365.85	371.63	376.16	378.44	386.30
λ (mW.m ⁻¹ .K ⁻¹)	17.44	18.25	18.95	19.51	19.92	19.94	20.95

T (K)	405.82	413.53	425.02	425.22	433.32	435.36	445.12
λ (mW.m ⁻¹ .K ⁻¹)	22.64	22.99	24.36	24.39	24.96	25.31	26.27

T (K)	450.00	453.91	454.51	465.02	465.25	473.26
λ (mW.m ⁻¹ .K ⁻¹)	26.71	26.78	26.89	27.97	27.90	28.42

Table II. Thermal conductivity of R134a along the quasi-isotherm 302 K

Temperature (K)	Pressure (MPa)	Density (kg.m ⁻³)	λ (mW.m ⁻¹ .K ⁻¹)	$\Delta_R\lambda$ (mW.m ⁻¹ .K ⁻¹)	$(\lambda_{exp} - \lambda_{cal})/\lambda_{exp}$ (%)
302.04	45.480	1348	105.23	92.08	- 0.26
302.70	44.200	1344	104.88	91.68	0.08
303.19	42.230	1338	104.20	90.95	0.33
303.37	38.160	1328	101.93	88.66	- 0.15
302.47	37.867	1329	101.96	88.77	- 0.27
302.64	36.011	1324	101.05	87.85	- 0.33
302.65	34.829	1321	100.49	87.29	-0.36
302.82	34.003	1319	99.96	86.74	- 0.47
303.34	26.970	1298	96.52	83.25	- 0.44
303.35	25.955	1295	96.01	82.75	- 0.44
303.36	24.969	1292	95.67	82.40	- 0.27
303.37	23.007	1286	94.52	81.25	- 0.42
303.38	22.003	1282	94.03	80.76	-0.38
303.82	8.028	1226	85.31	72.00	-0.39
303.83	6.997	1221	84.66	71.35	- 0.27
303.84	5.985	1216	83.88	70.57	- 0.29
303.86	4.975	1210	83.32	70.01	- 0.02
303.87	3.977	1205	82.44	69.13	-0.06
303.88	2.976	1199	81.70	68.38	0.02

303.39	1.985	1192	80.85	67.53	0.03
303.90	0.964	1186	80.10	66.79	0.26

Table III. Thermal conductivity of R134a along the quasi-isotherm 321 K

Temperature (K)	Pressure (MPa)	Density (kg.m ⁻³)	λ (mW.m ⁻¹ .K ⁻¹)	$\Delta_R\lambda$ (mW.m ⁻¹ .K ⁻¹)	$(\lambda_{exp}-\lambda_{cal})/\lambda_{exp}$ (%)
321.51	39.643	1290	96.70	81.79	- 0.67
321.52	39.020	1289	96.09	81.18	- 1.00
321.52	38.000	1286	96.69	80.79	0.00
321.53	37.021	1283	95.31	80.41	- 0.86
321.53	36.004	1280	94.92	80.00	- 0.78
321.54	35.000	1277	94.37	79.46	- 0.85
321.54	34.020	1274	93.99	79.08	- 0.76
321.55	33.014	1271	93.43	78.52	- 0.83
321.55	32.016	1268	92.87	77.95	- 0.91
321.56	31.010	1265	92.33	77.41	- 0.95
321.56	30.000	1262	91.82	76.90	- 0.95
321.57	29.023	1258	91.28	76.37	- 0.98
321.58	28.013	1255	90.75	75.84	- 0.99
321.58	27.022	1252	90.25	75.36	- 0.96
321.59	26.004	1248	89.73	74.81	- 0.93
321.59	25.001	1244	89.09	74.17	- 1.03
321.61	23.013	1237	87.90	72.98	- 1.11
321.77	22.002	1233	87.29	72.35	- 1.09
321.93	6.012	1149	75.93	60.98	- 1.04

321.95	4.000	1133	74.18	59.23	- 0.79
321.97	3.010	1124	73.53	58.58	- 0.28

Table IV. Thermal conductivity of R134a along the quasi-isotherm 331 K

Temperature (K)	Pressure (MPa)	Density (kg.m ⁻³)	λ (mW.m ⁻¹ .K ⁻¹)	$\Delta_R \lambda$ (mW.m ⁻¹ .K ⁻¹)	$(\lambda_{exp} - \lambda_{cal})/\lambda_{exp}$ (%)
330.64	40.070	1271	95.15	79.41	0.17
330.96	36.008	1258	93.61	77.85	0.68
330.97	33.856	1251	92.54	76.77	0.69
331.15	29.956	1238	90.48	74.70	0.72
331.15	29.007	1234	89.80	74.02	0.54
331.31	27.000	1226	88.74	72.94	0.65
331.32	25.914	1222	87.88	72.08	0.39
331.48	25.006	1218	87.44	71.63	0.54
331.64	24.000	1214	86.86	71.03	0.60
331.64	23.318	1211	86.40	70.57	0.55
331.80	22.261	1206	85.80	69.96	0.65
331.80	21.687	1203	85.35	69.51	0.55
331.81	20.234	1198	84.47	68.62	0.48
331.98	19.015	1191	83.50	67.64	0.45
331.98	18.014	1186	82.94	67.08	0.58
332.00	16.004	1175	81.56	65.70	0.61
331.86	15.005	1171	80.85	65.00	0.57
331.87	14.004	1165	80.05	64.20	0.50
331.88	13.003	1159	79.27	63.42	0.49

331.90	12.009	1153	78.51	62.66	0.53
331.90	11.007	1146	77.74	61.89	0.59

Table V. Thermal conductivity of R134a along the quasi-isotherm 349 K

Temperature (K)	Pressure (MPa)	Density (kg.m ⁻³)	λ (mW.m ⁻¹ .K ⁻¹)	$\Delta_R \lambda$ (mW.m ⁻¹ .K ⁻¹)	$(\lambda_{exp} - \lambda_{cal})/\lambda_{exp}$ (%)
349.06	38.017	1222	89.08	71.68	- 0.09
349.07	37.008	1219	88.50	71.09	- 0.17
349.08	36.000	1215	87.93	70.52	- 0.23
349.09	35.003	1212	87.53	70.13	- 0.09
349.09	34.000	1208	86.97	69.57	- 0.12
349.10	32.002	1200	85.89	68.49	- 0.13
349.11	30.951	1196	85.32	67.91	- 0.11
349.11	30.015	1192	84.81	67.40	- 0.09
349.12	29.014	1188	84.11	66.70	- 0.23
349.12	28.002	1184	83.59	66.18	- 0.15
349.13	27.014	1179	82.92	65.51	- 0.25
349.15	24.937	1170	81.61	64.20	- 0.30
349.31	22.001	1155	79.69	62.26	- 0.29
349.32	21.012	1149	79.06	61.64	- 0.23
349.32	20.001	1144	78.45	61.03	- 0.12
349.33	19.005	1138	77.71	60.28	- 0.17
349.34	18.008	1132	76.90	59.48	- 0.26
349.34	17.007	1126	76.40	58.97	0.05
349.36	16.000	1119	75.55	58.13	- 0.04

349.37	15.000	1112	74.83	57.40	0.06
349.38	14.003	1105	74.02	56.59	0.09

Table VI. Thermal conductivity of R134a along the quasi-isotherm 443 K

Temperature (K)	Pressure (MPa)	Density (kg.m ⁻³)	λ (mW.m ⁻¹ .K ⁻¹)	$\Delta_R\lambda$ (mW.m ⁻¹ .K ⁻¹)	$(\lambda_{exp} - \lambda_{cal})/\lambda_{exp}$ (%)
443.42	39.006	1008	72.56	46.61	- 0.12
443.30	38.020	1002	72.52	46.58	0.54
443.06	37.003	996.0	71.87	45.96	0.40
443.21	31.016	951.7	68.32	42.40	0.54
443.21	30.002	943.0	67.52	41.60	0.33
443.20	29.007	934.2	66.96	41.04	0.49
443.10	25.006	893.6	63.91	38.00	0.22
443.11	24.010	882.4	62.99	37.07	- 0.02
443.12	23.015	870.1	62.04	36.12	- 0.24
443.00	22.008	857.0	61.15	35.24	- 0.35
443.13	21.160	844.6	60.29	34.37	- 0.51
443.17	16.003	747.7	54.98	29.06	- 0.36
443.18	15.000	721.6	53.72	27.80	- 0.22
443.19	14.000	691.7	52.04	26.12	- 0.59
443.21	13.006	657.1	50.46	24.54	- 0.43
443.26	10.975	565.4	46.33	20.40	- 0.14
443.29	9.975	507.0	44.00	18.07	0.28
443.92	7.004	301.2	34.78	8.79	- 0.27
444.22	5.946	235.6	32.31	6.29	- 0.25

444.26	5.006	185.1	30.65	4.64	0.00
445.11	0.731	20.87	26.62	0.53	0.51

Table VII. Thermal conductivity of R134a along the quasi-isotherm 463 K

Temperature (K)	Pressure (MPa)	Density (kg.m ⁻³)	λ (mW.m ⁻¹ .K ⁻¹)	$\Delta_R\lambda$ (mW.m ⁻¹ .K ⁻¹)	$(\lambda_{exp} - \lambda_{cal})/\lambda_{exp}$ (%)
463.67	39.531	966.0	70.71	42.94	- 0.31
463.55	39.000	962.7	70.35	42.58	- 0.44
463.56	38.020	955.9	69.77	42.01	- 0.50
463.44	37.021	949.0	69.72	41.97	0.21
463.32	36.007	941.7	69.09	41.35	0.12
463.33	35.009	934.0	68.54	40.79	0.15
463.33	34.010	925.9	67.96	40.21	0.19
463.21	33.001	917.8	67.13	39.40	- 0.15
463.22	32.000	909.0	66.60	38.87	- 0.03
463.10	31.00	900.2	65.81	38.09	- 0.28
463.11	30.005	890.6	65.29	37.56	- 0.09
463.11	29.007	880.6	64.54	36.81	- 0.23
463.12	28.015	870.1	63.59	35.86	- 0.66
463.12	27.015	858.9	62.86	35.14	- 0.69
463.13	26.018	847.2	62.16	34.44	- 0.66
463.01	25.012	834.9	61.48	33.76	- 0.55
463.02	24.001	821.4	60.63	32.92	- 0.63
462.96	16.000	666.1	52.58	24.87	- 0.62
462.98	15.009	636.6	51.15	23.44	- 0.68

462.87	14.011	603.6	49.63	21.93	- 0.62
462.88	13.506	584.9	48.79	21.08	- 0.61
462.89	13.003	565.2	47.92	20.22	- 0.50
462.90	12.473	542.9	47.00	19.29	- 0.33
462.92	12.003	522.0	45.96	18.25	- 0.52
462.93	11.505	498.62	45.10	17.39	- 0.09
463.06	11.007	473.6	44.02	16.30	0.00
463.07	10.500	447.48	43.01	15.28	0.35
463.20	10.006	420.8	41.84	14.11	0.38
463.24	8.995	365.6	39.29	11.55	0.00
463.38	8.725	350.5	38.72	10.97	0.14
463.90	7.497	283.6	35.8	8.05	- 0.39
464.17	6.500	233.4	33.95	6.12	- 0.51
464.44	5.758	198.65	32.77	4.92	- 0.48
464.44	5.533	188.66	32.51	4.67	- 0.26
464.68	5.401	182.7	32.40	4.54	- 0.62
464.45	5.397	182.73	32.39	4.55	- 0.30
464.82	5.258	176.42	32.22	4.34	- 0.04
464.83	5.000	165.56	31.85	3.97	- 0.13
464.83	4.750	155.29	31.41	3.58	- 0.52
465.07	4.577	148.2	31.36	3.46	- 0.08
465.32	4.226	134.29	31.00	3.08	- 0.02

465.33	3.75	116.43	30.31	2.39	- 0.65
465.33	3.486	106.87	30.26	2.33	0.00
465.33	3.02	90.57	29.99	2.06	0.46
465.03	0.646	17.49	28.32	0.42	0.35

Table VIII: Thermal conductivity of R134a along the critical isochore

Temperature (K)	λ (exp.) (mW.m ⁻¹ .K ⁻¹)	λ (Krauss) (mW.m ⁻¹ .K ⁻¹)	$\Delta_c\lambda$ (mW.m ⁻¹ .K ⁻¹)	$\Delta_c\lambda$ (Krauss) (mW.m ⁻¹ .K ⁻¹)
374.53	97.03	140.25	59.51	114.88
375.66	82.89	73.21	45.37	47.78
376.64	72.17	62.29	34.65	36.80
377.88	66.50	55.80	28.98	30.30
378.43	63.75	53.95	26.23	28.34
380.74	57.49	49.15	19.97	23.38
384.37	51.57	45.53	14.05	19.52
393.62	46.50	42.04	8.97	15.43
403.46	44.67	40.77	7.15	13.54